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ABSTRACT

Neutron hardening and embrittlement of pressure vessel steels is due to a high density of nanometer scale features, including Cu-rich precipitates which form as a result of radiation enhanced diffusion. High-energy displacement cascades generate large numbers of both isolated point defects and clusters of vacancies and interstitials. The subsequent clustering, diffusion and ultimate annihilation of primary damage is inherently coupled with solute transport and hence, the overall chemical and microstructural evolutions under irradiation. In this work, we present atomistic simulation results, based on many-body interatomic potentials, of the migration of vacancies, solute and self-interstitial atoms (SIA) in pure Fe and binary Fe-0.9 and 1.0 at.% Cu alloys. Cu diffusion occurs by a vacancy mechanism and the calculated Cu diffusivity is in good agreement with experimental data. Strain field interactions between the oversized substitutional Cu solute atoms and SIA and SIA clusters are predominantly repulsive and result in both a decreased activation energy and diffusion pre-factor for SIA and small ($N <5$) SIA cluster migration, which occurs by three-dimensional motion. The Cu appears to enhance the re-orientation of the SIA clusters to different <111> directions, as well as the transition from <110> to mobile <111> configurations. The migration behavior of larger SIA clusters, which undergo only one-dimensional diffusion during molecular dynamics timescales, is largely unaffected by the Fe-Cu alloy, although SIA clusters are effectively repelled by coherent Cu precipitates.

INTRODUCTION

It is well established that radiation embrittlement of western reactor pressure vessel (RPV) steels results from the formation of a high number density of small ($r<2$ nm), coherent Cu-rich precipitates during neutron irradiation [1-3]. The precipitates form as a consequence of radiation enhanced diffusion of supersaturated Cu and impede dislocation glide, producing yield strength increases that are responsible for embrittlement [2]. A number of groups have used theoretical, experimental and computational techniques, including kinetic Monte Carlo simulations, to study the evolution of Cu precipitates during irradiation and thermal aging [4-7]. Yet, a quantitative assessment of Cu diffusivity at reactor operating temperatures around 300°C is lacking, though it is an important and required input to integrated, multiscale models of radiation embrittlement. Additionally, it is important to understand the effect of solutes and precipitates on the dynamical behavior of self-interstitial atoms (SIA) and SIA clusters from a

fundamental, atomic-level perspective and to determine the implications of such behavior to the overall-mesoscale, microstructural evolution. In this paper, we report results of a molecular dynamics (MD) study to provide fundamental insight into both solute migration and the diffusion of SIA and small SIA clusters in pure Fe and binary Fe-Cu alloys containing both dissolved solute atoms and coherent Cu precipitates. The simulations were carried out using the MDCASK code [8], based on the many-body, Fe-Cu potentials of Ackland *et al.* [9].

RESULTS

<u>Vacancy and solute diffusion</u>

   Substitutional Cu in dilute solution in b.c.c. alloys is known to diffuse through a vacancy mechanism. In irradiated alloys, primary damage production by high energy displacement cascades results in excess vacancy production. These vacancies provide the necessary solute enhanced diffusion for supersaturated alloy systems to reach thermodynamic equilibrium by the formation of a high number of nanoscale Cu precipitates. Comprehensive, microstructural evolution models of phase decomposition kinetics require an accurate assessment of both the thermal and radiation enhanced solute diffusion coefficients. Atomistic simulations offer the possibility to directly calculate the required migration properties. However, due to the inherent computational limits of MD simulations, obtaining statistically significant vacancy diffusion data is difficult at all but very high temperatures. In order to improve the statistical accuracy of vacancy-Cu diffusion calculations, we have performed simulations with vacancy concentrations far in excess of thermal equilibrium values and temperatures ranging from 1000 to 1750 K. While these initial results are obtained under quite extreme conditions, the calculations will be extended to more realistic vacancy concentration and temperature ranges.

   Cu atom diffusion simulations were performed in a 16,000 atom ($20a_o \times 20a_o \times 20a_o$) supercell with a MD timestep of 1.5 fs and 0.9 at. % Cu (145 Cu atoms) with vacancy concentrations of 0.001, 0.05 and 0.01, i.e. containing 16, 80 and 160 vacancies respectively. The Cu diffusion coefficient was calculated from the Cu-atom mean square displacement during simulations of 0.6 to 2.1 nanoseconds in duration. The calculated Cu diffusivities were then corrected to the equilibrium vacancy concentration using the relation, $D_{Cu}(C_{eq}) = C_{eq} \cdot D_{Cu}(C_v)/C_v$, where D_{Cu} is the solute diffusivity, C_v the vacancy concentration in the simulation and C_{eq} the equilibrium vacancy concentration for an Fe-0.9% Cu alloy [10]. In the case of the two highest vacancy concentrations, some three dimensional, vacancy-Cu clusters formed. While Wirth and Odette have proposed that small, copper-vacancy clusters are mobile based on pair- and EAM-potential models used in kinetic Monte Carlo simulations [11], the mobility of such clusters is considerably less than that of individual vacancies and, these clusters remain essentially frozen in place during the MD simulation timescales. Thus, following their formation, the three-dimensional vacancy-Cu aggregates do not contribute to the overall Cu diffusion and, to first order, these vacancies can simply be subtracted from the total vacancy contribution for purposes of correcting the Cu diffusivity to the equilibrium vacancy concentration. While not rigorously accurate, the resulting copper diffusion coefficients calculated in this manner all lie on a single, exponential line in the Arrhenius diagram shown in Figure 1.
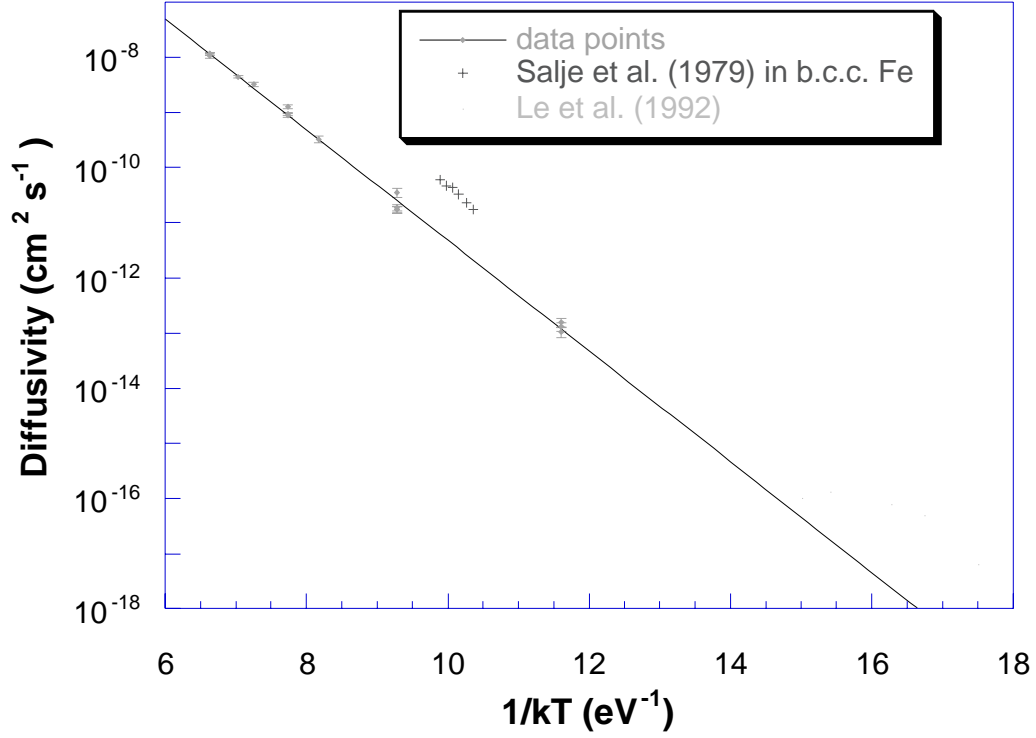
Figure 1. *Cu solute diffusion coefficient in a Fe-0.9 at. % Cu alloy compared to several experimental results. Data points have been derived after correction from different vacancy concentrations. Experimental data from Lê et al. [12] and Salje et al. [13] is included.*

The exponential fit to the data in Figure 1 results in a temperature-dependent Cu diffusion coefficient in a Fe-0.9 at.% Cu alloy of $D_{Cu}(T)=5.2\times10^{-2}\exp(-2.31/kT)$ (cm^2 s^{-1}). Since the Cu diffusion data was corrected to the equilibrium vacancy concentration, the vacancy formation energy of approximately 1.69 eV in a Fe-0.9 at.% Cu alloy must be subtracted to obtain the Cu migration energy. Thus, we obtain a Cu migration energy of E_m=0.62 eV.

SIA diffusion

SIA diffusion simulations were performed in a $10a_o\times10a_o\times10a_o$ simulation cell at temperatures ranging from 600 to 1200 K for times up to 1 ns in α-Fe and in Fe-1.0 at.% Cu. In each case, the defect diffusivity was calculated from its mean square displacement [14]. In pure Fe, the resulting temperature dependent SIA diffusion coefficient is $D_{SIA-Fe}(T)=1.9\times10^{-3}\exp(-0.13/kT)$ (cm^2 s^{-1}), whereas in Fe-1.0%Cu, $D_{SIA-FeCu}(T)=1.2\times10^{-3}\exp(-0.09/kT)$ (cm^2 s^{-1}). These results have a statistical uncertainty of about 10%. The decrease in both effective activation energy and diffusion pre-factor are notable and can be explained by the strain field interactions between the oversized Cu solute atom and the self-interstitial and are described in more detail elsewhere [14]. In the vicinity of oversized Cu atoms the relative SIA energies are shifted slightly in favor of orientations away from those nearest to the <110> and, to a lesser extent, <111> directions. This results in an effectively decreased activation energy for rotation from the <110> to the <111> configuration and a net increase in the probability of the <110>-to-<111>

re-orientation step required for SIA diffusion [15]. At the same time, the rotation rate in the opposite direction (<111> to <110>) is also enhanced. The first process results in a lower activation energy for SIA migration, while the latter effect decreases the pre-exponential factor. Figure 2 shows the probability distribution of observing the SIA in the different orientations that lie between the stable <110> and the <111> split dumbbell, obtained during 40 ps of simulation at 400 K.
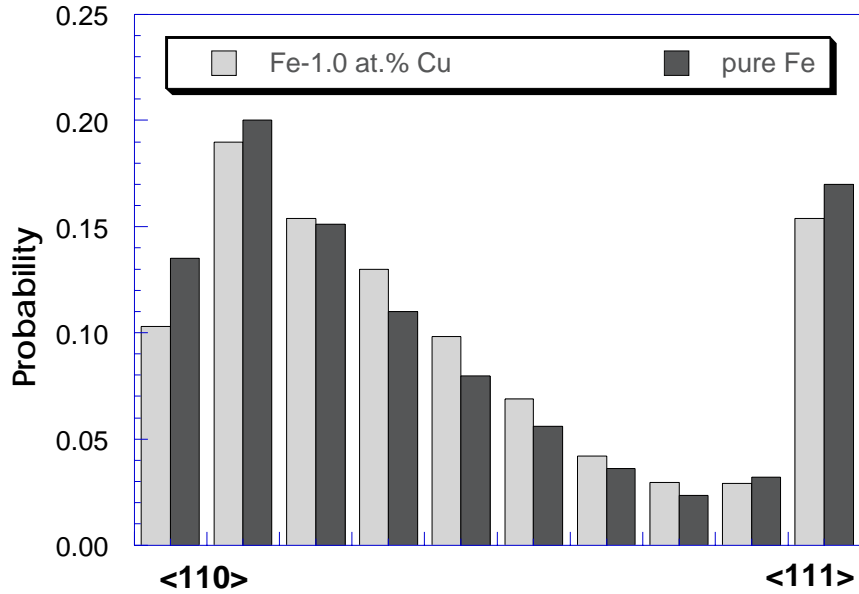
Figure 2. Probabilityof observing a SIA in orientations abetween <110> and <111> both in pure Fe and in Fe-1.0 at.% Cu, obtained from 40-ps MD simulations at 400 K. The higher probability for orientations between <110> and <111> configurations in Fe-Cu indicates enhanced SIA rotations.

Similar simulations were performed for a 3-member SIA cluster. Analysis of the cluster mean square displacement yielded values of $D_o=1.35\times10^{-3}$ cm^2 s^{-1} and $D_o=5.50\times10^{-4}$ cm^2 s^{-1} for the pre-factor and values of 0.07 eV and 0.04 eV for the migration energy in Fe and Fe-Cu, respectively. Again, the effect of Cu is to decrease the SIA cluster diffusion parameters. Small SIA clusters in pure Fe consist of <111>-oriented split dumbbells and crowdions, which undergo rapid one-dimensional migration. However, the overall migration behavior of small SIA clusters is three-dimensional and results from rotations between differently orientated <111> configurations. In the case of the Fe-Cu alloy, the difference in E_m can be attributed to enhanced re-orientations between <111> cluster orientations, resulting again from repulsive Cu-SIA cluster strain field interactions. We ascribe the difference in D_o to the fact that shorter <111> one-dimensional jump trajectories and more rotation are observed in the Fe-Cu alloy, resulting in less *effective* diffusion. Figure 3 shows the center of gravity trajectory of a 3-SIA during 0.6 ns at 1000 K in both pure Fe and in the Fe-1.0 at.% Cu alloy. Thus, the effect of Cu is to shorten the jump sequences and increase the frequency of directional re-orientations.
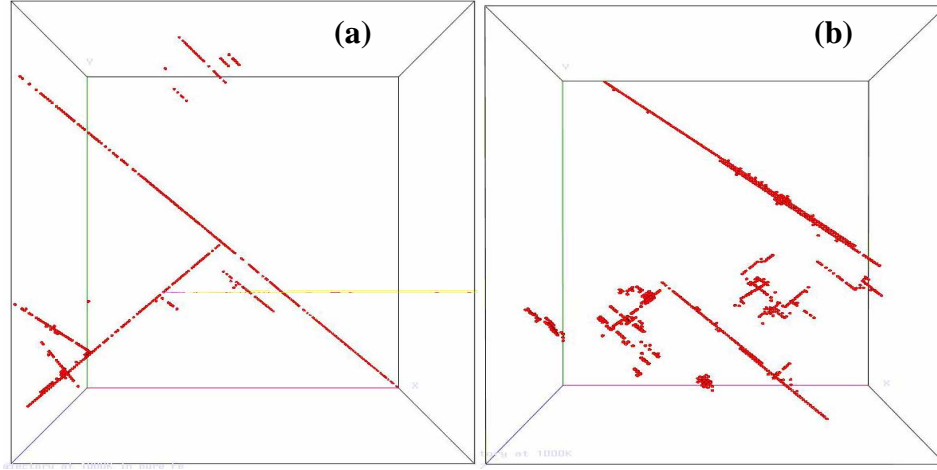
Figure 3. *3-SIA center of gravity diffusion trajectory during 0.6 ns at 1000 K in (a) Fe and (b) FeCu. Note the more frequent changes in direction and shorter <111> diffusion lengths in FeCu. At lower temperatures, and during MD accesible timescales, no change in direction is observed and the 3-SIA performs a fully one-dimensional random walk.*

Slightly larger SIA clusters undergo only one-dimensional diffusion during molecular dynamics timescales. In our simulations, a 10-SIA executes a fully one-dimensional random walk, without directional changes in both pure Fe and the Fe-Cu alloy. The effective migration energy is the same (0.05 eV) in both cases. However, as for 3-SIA cluster diffusion, the effect of Cu is to shorten the length of the <111> cluster jump segments. This results in a decreased pre-factor in the Fe-Cu alloy, and we obtained values of $D_o(\text{FeCu})=1.10\times10^{-3}$ cm^2 s^{-1} versus $D_o(\text{Fe})=2.20\times10^{-3}$ cm^2 s^{-1}.

Finally, it is also important to consider the interaction between one-dimensionally gliding SIA loops with nanometer-sized Cu precipitates which form in RPV steels. To address this possibility, we report the results of preliminary simulations of the interaction between a 2-nm-diameter spherical Cu precipitate and a 10-SIA cluster whose glide prism intersected the precipitate. During approximately 250 ps at 560 K, the SIA cluster remained *effectively* trapped between the precipitate and its periodic mirror image (MD periodic boundary conditions). Further, a molecular-statics analysis of the interaction energy reveals the existence of an energy barrier for the propagation of the cluster into the precipitate, as expected by consideration of the strain field interactions between the precipitate and interstitial cluster. However, the calculations also show that if the SIA cluster enters the precipitate it becomes trapped and, more importantly, is composed entirely of Cu atoms. Thus, even if the SIA clusters are absorbed, they do not inject Fe atoms into the precipitate.

CONCLUSIONS AND ACKNOWLEDGEMENTS

Solute and SIA diffusion in Fe-0.9 and 1.0 at.% Cu alloys has been studied by atomistic simulation. A Cu migration energy of 0.62 eV has been found, in good agreement with some experimental results. The effect of oversized substitutional Cu solute atoms on nearby SIA and small SIA clusters is to change the configuration-dependent energies as a result of strain field interactions. The resulting effect on diffusional properties is two-fold. First, the altered SIA configuration-dependent energies result in enhanced rotation between <110> and <111> configurations for SIAs and between different <111> configurations for SIA clusters, and a decreased effective activation energy for migration. Second, they also result in shorter sets of correlated <111> jump sequences and a decreased diffusion pre-factor. While the change in the diffusion parameters is not very significant , the enhancement of three- versus one-dimensional migration for SIA clusters may be quite relevant. Hence, extension of this calculations to larger cluster sizes and longer simulation times is an important objective.

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